(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 866 095 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
23.09.1998 Bulletin 1998/39

(51) Int. Cl.[6]: **C08L 39/00**, D21C 9/16, C08K 5/14, C08K 3/20

(21) Application number: **98104260.9**

(22) Date of filing: **10.03.1998**

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **13.03.1997 IT MI970565**

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(54) *Compositions for bleaching paper*

(57) Compositions for bleaching paper produced from cellulose, which comprise solutions, suspensions or dispersions of hydrogen peroxide and a polydiallyldialkylammonium salt in reciprocal weight ratios varying from about 5:1 to about 70:1. Suspensions of cellulose containing the compositions of the invention and processes for preparing the same. Use of the compositions in the processes of production of paper from cellulose. These compositions allows to keep constant the degree of whiteness of the paper along its manufacture.

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Description

The present invention refers to compositions comprising hydrogen peroxide and a polydiallyldialkylammonium salt, and their use as additives in the paper and cellulose industry.

The use of the compositions according to the invention allows to keep constant the degree of whiteness of the paper produced from cellulose, substantially independently from the amounts of lignin it contains.

Through well known procedures, cellulose is obtained almost exclusively from wood, which is mainly composed of lignin, a brown non-fibrous substance, and cellulose. The procedures essentially consist in the separation of these two components and in the subsequent, more or less drastic purification of the cellulose thus obtained.

The common feature of the different procedures is the digestion of wood in a solution of an agent (e.g. sodium hydroxide, sodium sulphite) capable of dissolving lignin by transforming it into one of its water-soluble derivatives in order to separate it from cellulose in the form of an aqueous solution. The cellulose, which is left undissolved and separated, is subsequently washed to remove most of the residual foreign substances among which, as an example, the compounds resulting from the degradation of lignin.

However, the cellulose thus obtained still contains more or less significant residues of lignin; hence, it must be further purified before being employed in the production of paper suitable for most uses.

By means of subsequent treatments, the residual lignin is removed or transformed into colorless compounds through "bleaching" procedures.

Bleaching is an oxidation reaction and can be performed according to two different methods, by employing, as the oxidizer, chlorine, generally in the form of sodium or calcium hypochlorite, or oxygen, which can also be in the form of ozone or, generally, hydrogen peroxide.

Normally, the best cellulose is obtained by oxidation with chlorine (hypochlorite). This procedure, however, has several drawbacks, one of them being represented by the waste waters containing large amounts of chlorides, corrosive to the plants, and small amounts of organic chlorinated substances; in view of this, due to ecological reasons, it is difficult to dispose of said waters which, practically, cannot be recycled.

For these reasons, the procedure which is presently employed almost exclusively is that based on oxygen, generally in the form of hydrogen peroxide, though the quality of the cellulose is lower than that obtained with the chlorine-based method.

Depending on the type of trees as well as the place of origin, the amount of lignin in wood varies within sufficiently wide limits. As a consequence, and in spite of the purification operations described above, some residual lignin always remains, as such or in the form of a corresponding salt, the amount of which varies depending on the typ of wood and the purification procedure (generally, from about 10 to about 800 ppm).

The variability of the content of lignin in the cellulose creates serious problems to paper mills.

As a matter of fact, during the proces of production of paper, immediately before the formation of the sheet on the machine wire, a retentive agent is added to the cellulose suspension, generally a cationic polymer. The residual lignin present in the cellulose, generally as a soluble sulfonate, forms with the cationic polymer a water-insoluble polymeric salt and hence, it precipitates, at least partially, in the form of a yellow solid.

This solid, being mixed with the cellulose during the formation of the sheet, makes it more or less yellow, depending on its amount and the precipitated portion.

It follows that, during the production, it is not possible to keep constant the degree of whiteness of the produced paper without spending a lot of time and energy, in view of the fact that, often, one has to interrupt the production, change the production conditions and the amounts of auxiliary agents for bringing the whiteness degree back to the original value, thus generating undesidered production wastes.

Normally, any lignin that is present in the cellulose suspension is not quantitatively precipitated and, as a consequence, a portion remains undissolved in the waste waters. The latter are always recycled, possibly after a simple clarification process, and, therefore, the dissolved lignin adds to that contained in the following cellulose charge; in view of this, in extreme cases, lignin can continue to accumulate and, as a consequence, a continuous lowering of the degree of whiteness is observed.

The whiteness degree might also improve if the subsequent charges of cellulose contained considerably lower amounts of lignin, but even any possible increase in the whiteness degree, being a variation, would consitute a problem for the production as well.

The problem of this variation during the production becomes particularly serious when, as it often happens, an optical bleacher is used during the production in order to achieve a given and desired degree of whiteness which, of course, must remain unchanged for the entire production time. Therefore, the problem which has to be solved is not, actually, the availability of a cellulose of such a quality to allow the achievement of a high whiteness degree (which might be attained, in any case, by increasing the amount of optical bleacher), rather that of making it possible to keep unchanged the starting predetermined whiteness degree.

It would be advisable to eliminate completely the lignin which is present in the suspension of cellulose before the formation of the sheet, or see to it that the amount of lignin which precipitates upon addition of the retentive agent is always constant. Attempts to quantitatively degrade lignin through further oxidation by means of hydrogen peroxide or peracetic acid in the "pulper"

hav been carried out. However, the results are not satisfactory and the problem remains unsolved.

Surprisingly, it has been found that, by adding small quantities of a composition comprising hydrogen peroxide and a polydiallyldialkylammonium salt to the cellulose suspension in the "pulper" or in any other suitable part of the plant, it is possible to keep constant the whiteness degree of the paper substantially independently from the amount of lignin contained in the cellulose, thus solving the severe production problems. It has also been found that the constancy of the whiteness degree is mantained also when an optical bleaching agent is used in the production process.

The compositions according to the invention are solutions, dispersions or suspensions of hydrogen peroxide and a polydiallyldialkylammonium salt in a liquid vehicle, in which the reciprocal weight ratios hydrogen peroxide : polydiallyldialkylammonium salt are comprise between about 5:1 and about 70:1.

In such compositions, the total amount of the hydrogen peroxide and the polydiallyldialkylammonium salt represents from about 1% to about 65% of the weight of the composition and, preferably, from about 10% to about 50%.

In a preferred embodiment, the liquid vehicle is water and the compositions are solutions of hydrogen peroxide and of a polydiallyldialkylammonium salt, in which the reciprocal weight ratios hydrogen peroxide : polydiallyldialkylammonium salt are as above indicated, and the polydiallyldialkylammonium salt is polydiallyldimethylammonium chloride. The type and the amount of composition of the invention which is added to the cellulose suspension depends on the nature of the wood which is employed for the preparation of said suspension and the way the pulp is worked for removing most of lignin. Thus, still a further object of the present invention is represented by suspensions of cellulose added with the compositions of the invention. Preferably, these suspensions are added with the compositions according to the invention so as to have in the suspension a total amount of hydrogen peroxide and the selected polydiallyldialkylammonium salt varying from about 0.01% to about 5% of the weight of the cellulose suspension.

Finally, another object of the present invention is represented by a process for the preparation of the above mentioned cellulose suspensions, which comprises the addition of a composition of the invention to a cellulose suspension containing sulfonated lignin in amounts comprised between about 10 and about 800 part per million (ppm), so as to obtain a suspension in which the total amount of hydrogen peroxide and the polydiallyldialkylammonium salt varies from about 0.01% and about 5% of the weight of the suspension. For the purposes of the present invention, the composistion can also be prepared in situ by separately adding to the cellulose suspension, in whichever order, hydrogen peroxide and the selected polydiallyldialkylammonium salt or the solutions, suspensions or dispersions of hydrogen peroxide and the selected polydiallyldialkylammonium salt, respectively.

The use of the polydiallyldialkylammonium salts as retentive agents in the manufacture of paper from cellulose, by adding them immediately before the formation of the sheet, has been known for a while.

Also the use of the polydiallyldialkylammonium salts in the final step of purification in the process of production of cellulose from wood is known.

However, the use of the compositions of the present invention to keep constant the degree of whiteness of the paper during its production is new and surprising.

The polydiallyldialkylammonium salts are commercial products. They can also be prepared as desribed in US Patent 3,288,770. Polydiallyldimethylammonium chloride is commercially available as CONDITIONER P6 (3V SIGMA, Bergamo, Italy).

The following examples illustrate the invention.

EXAMPLE 1

100 Grams of a 3% suspension of bleached cellulose are diluted to 0.5% with water and added with a 1 g of a 1.5% solution of the retentive agent FIBRAFFIN® K5 (cationic starch, Südstärke GmbH). The resulting mixture is stirred for 2-3 minutes, then the sheet is formed, which is subsequently dried at 90°C.

By operating in the same way, sheets are prepared from a suspension of cellulose containing different amounts of sodium ligninsulfonate (LSS) therein dissolved. Then, the degree of whiteness of the sheets is measured by means of an ELREPHO® 2000 reflection spectrophotometer (Datacolor).

The degrees of whiteness are reported in Table 1

TABLE 1

Sheet	LSS content ppm	Degree of whiteness
1	----	90.3
2	50	87.1
3	100	85.8
4	200	84.2

EXAMPLE 2

100 Grams of a 3% suspension of bleached cellulose are added with 0.2 g of 35% hydrogen peroxide, the whole is stirred for 30 minutes at 40°C, then the suspension is diluted with water to 0.5% and, from this point onwards, the same operations as those described in Example 1 are carried on.

The degrees of whiteness are reported in Table 2

TABLE 2

Sheet	LSS content ppm	Degree of whiteness
1	----	90.4
2	50	87.4
3	100	85.9
4	200	84.6

EXAMPLE 3

95 Grams of 35% hydrogen peroxide and 5 g of an aqueous 40% solution of polydiallyldimethylammonium chloride are mixed at room temperature.

100 Grams of a 3% suspension of bleached cellulose are added with 0.2 g of the above prepared mixture. The whole is stirred for 30 minutes at 40°C, the suspension is diluted with water to 0.5% and, from this point onwards, the same operations as those described in Example 1 are carried on.

The degrees of whiteness are reported in Table 3

TABLE 3

Sheet	LSS content ppm	Degree of whiteness
1	----	90.1
2	50	87.2
3	100	87.0
4	200	87.1

EXAMPLE 4

100 Grams of a 3% suspension of bleached cellulose are added with an aqueous 0.6% solution of the sodium salt of 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethylamino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-benzenesulfonic acid (OPTIBLANC® NL, optical bleaching agent by 3V SIGMA, Bergamo, Italy). The whole is stirred for 5 minutes, then the resulting suspension is diluted with water to 0.5% and, from this point onwards, the same operations as those described in Example 1 are carried on.

The degrees of whiteness are reported in Table 4

TABLE 4

Sheet	LSS content ppm	Degree of whiteness
1	----	103.4
2	50	101.6
3	75	100.4

TABLE 4 (continued)

Sheet	LSS content ppm	Degree of whiteness
4	150	99.5

EXAMPLE 5

98 Grams of 35% hydrogen peroxide and 2 g of an aqueous 40% solution of polydiallyldimethylammonium chloride are mixed.

100 Grams of a 3% suspension of bleached cellulose are added with 0.2 g of the above prepared mixture, then the whole is stirred for 30 minutes at 40°C, subsequently added with an aqueous 0.6% solution of the sodium salt of 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethylamino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-benzenesulfonic acid (OPTIBLANC® NL), and the mixture is stirred for 5 minutes. The resulting suspension is diluted with water to 0.5% and, from this point onwards, the same operations as those described in Example 1 are carried on.

The degrees of whiteness are reported in Table 5

TABLE 5

Sheet	LSS content ppm	Degree of whiteness
1	----	102.4
2	50	101.3
3	75	101.2
4	150	101.2

Claims

1. Compositions comprising hydrogen peroxide and a polydiallyldialkylammonium salt in a liquid vehicle.

2. Compositions as defined in claim 1, which are solutions, dispersion or suspensions.

3. Compositions as defined in claims 1 and 2, in which the weight ratios hydrogen peroxide : polydiallyldialkylammonium salt are comprised between about 5 : 1 and about 70 : 1.

4. Compositions as defined in claims from 1 to 3, in which the polydiallyldialkylammonium salt is polydiallyldimethylammonium chloride.

5. Compositions as defined in claims from 1 to 3, in which the liquid vehicle is water.

6. Compositions as defined in claims from 1 to 5, which are solutions.

7. Compositions as defined in claims from 1 to 6, in

which the total amount of hydrogen peroxide and the polydiallyldialkylammonium salt represents from about 1 to abut 65% of the weight of the composition.

8. Compositions as defined in claim 7, in which the total amount of hydrogen peroxide and the polydiallyldialkylammonium salt represents from about 10 to abut 50% of the weight of the compositions.

9. Compositions as defined in claims 7 and 8, in which the polydiallyldialkylammonium salt is polydiallyldimethylammonium chloride.

10. Compositions as defined in claims from 7 to 9, which are solutions.

11. Suspension of cellulose comprising compositions as defined in any of claims from 1 to 10.

12. Suspensions of cellulose as defined in claim 11, characterized in that they contain from about 10 to about 800 parts per million of sulfonated lignin.

13. Suspensions of cellulose as defined in claims 11 and 12, in which the total amount of hydrogen peroxide and the polydiallyldialkylammonium salt varies from about 0.01% to about 5% of the weight of the suspensions.

14. Suspensions of cellulose as defined in claim 13, in which the polydiallyldialkylammonium salt is poiydiallyldimethylammonium chloride.

15. Suspensions of cellulose as defined in any of claims 11 to 14, characterized in that they contain an optical bleaching agent.

16. A process for preparing suspensions of cellulose as defined in claim 11, which comprises adding to the suspensions compositions as defined in any of claims 1 to 10, so as to obtain suspensions in which the total amount of hydrogen peroxide and the polydiallyldialkylammonium salt varies from about 0.01% to about 5% of the weight of the suspensions.

17. A process as defined in claim 16, in which the suspensions of cellulose to which the compositions are added contain from about 10 to about 800 parts per million of sulfonated lignin as such or in the form of a corresponding salt.

18. A process as defined in claims 16 or 17, in which the polydiallyldialkylammonium salt is polydiallyldimethylammonium chloride.

19. A process as defined in claims from 16 to 18, in which the compositions of the invention are formed in situ by adding to the suspensions of cellulose hydr gen peroxide and the polydiallyldialkylammonium salt, or the corresponding single solutions, suspensions or dispersions, in whichever order.

20. Use of the compositions as defined in any of the claims from 1 to 10 in the processes of manufacture of paper from cellulose.

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EUROPEAN SEARCH REPORT

Application Number
EP 98 10 4260

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 493 987 A (BETZ EUROP INC) 8 July 1992 * page 4, line 20 - line 50 * * claims 1,5,12 *	1-10	C08L39/00 D21C9/16 C08K5/14 C08K3/20
A	* the whole document *	11-20	
X	DE 41 31 992 A (WELLA AG) 1 April 1993 * page 3, line 1 - line 30 * * claims 1,3,5 *	1-10	
A	* the whole document *	11-20	
A	EP 0 628 658 A (CALGON CORPORATION) 14 December 1994 * page 5, line 25 - page 6, line 5 *	1-14, 16-20	
A	US 4 217 425 A (BALLWEBER EDWARD G ET AL) 12 August 1980 * the whole document *	1-14, 16-20	
A	EP 0 148 712 A (ATOCHEM) 17 July 1985 * the whole document *	1-14, 16-20	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	WO 95 13421 A (ATOCHEM ELF SA) 18 May 1995 * the whole document *	1-14, 16-20	C08L D21C C08K
A	GB 1 119 221 A (MONSANTO COMPANY) 10 July 1968 * page 1, line 10 - line 18 * * page 1, line 63 - line 67 *	15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	20 May 1998	Naeslund, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
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D : document cited in the application
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